Sampling and preconcentration techniques for environmental radioactivity analysis

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Sampling & preconcentration techniques for environmental radioactivity analysis

Sampling techniques

- Air
- Soil
- Water
- Sediments

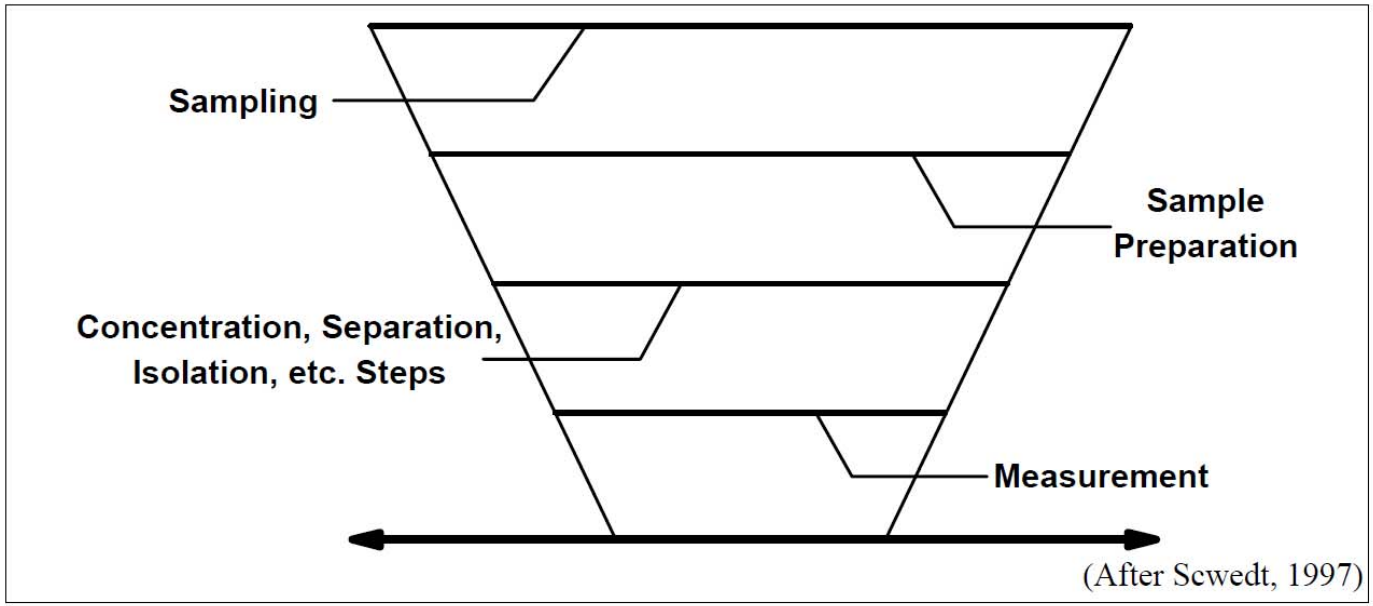
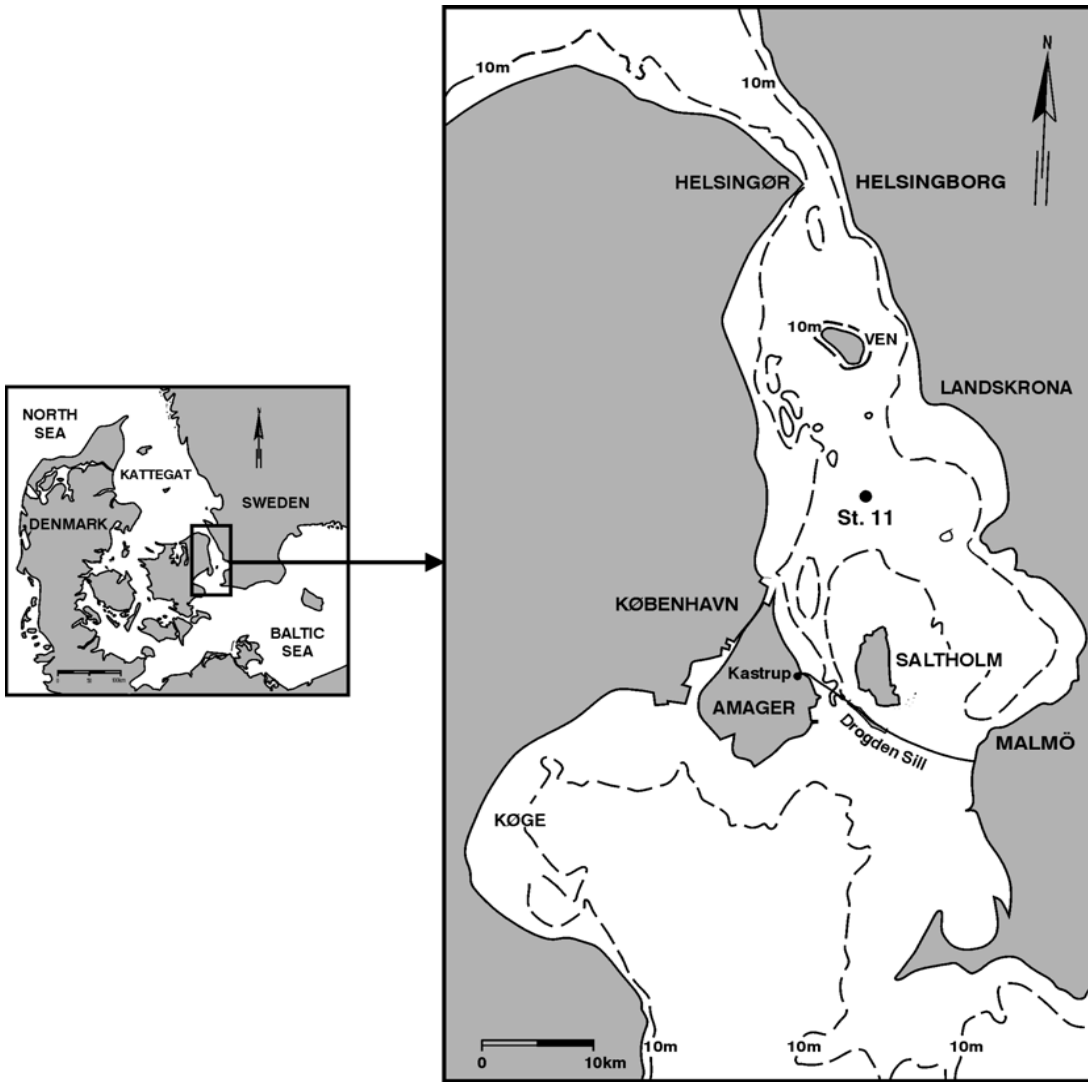
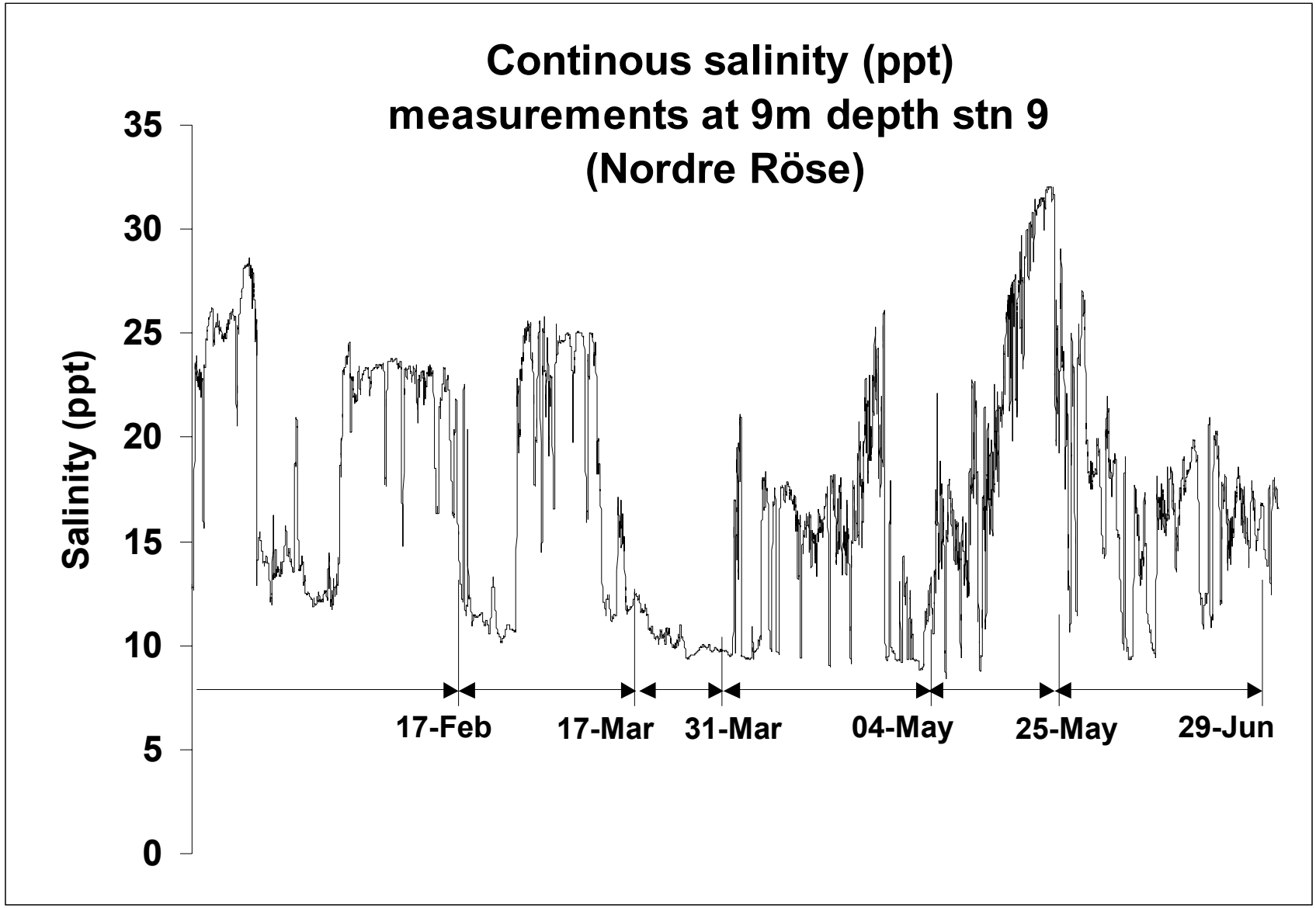


FIGURE 12.1—Degree of error in laboratory sample preparation relative to other activities

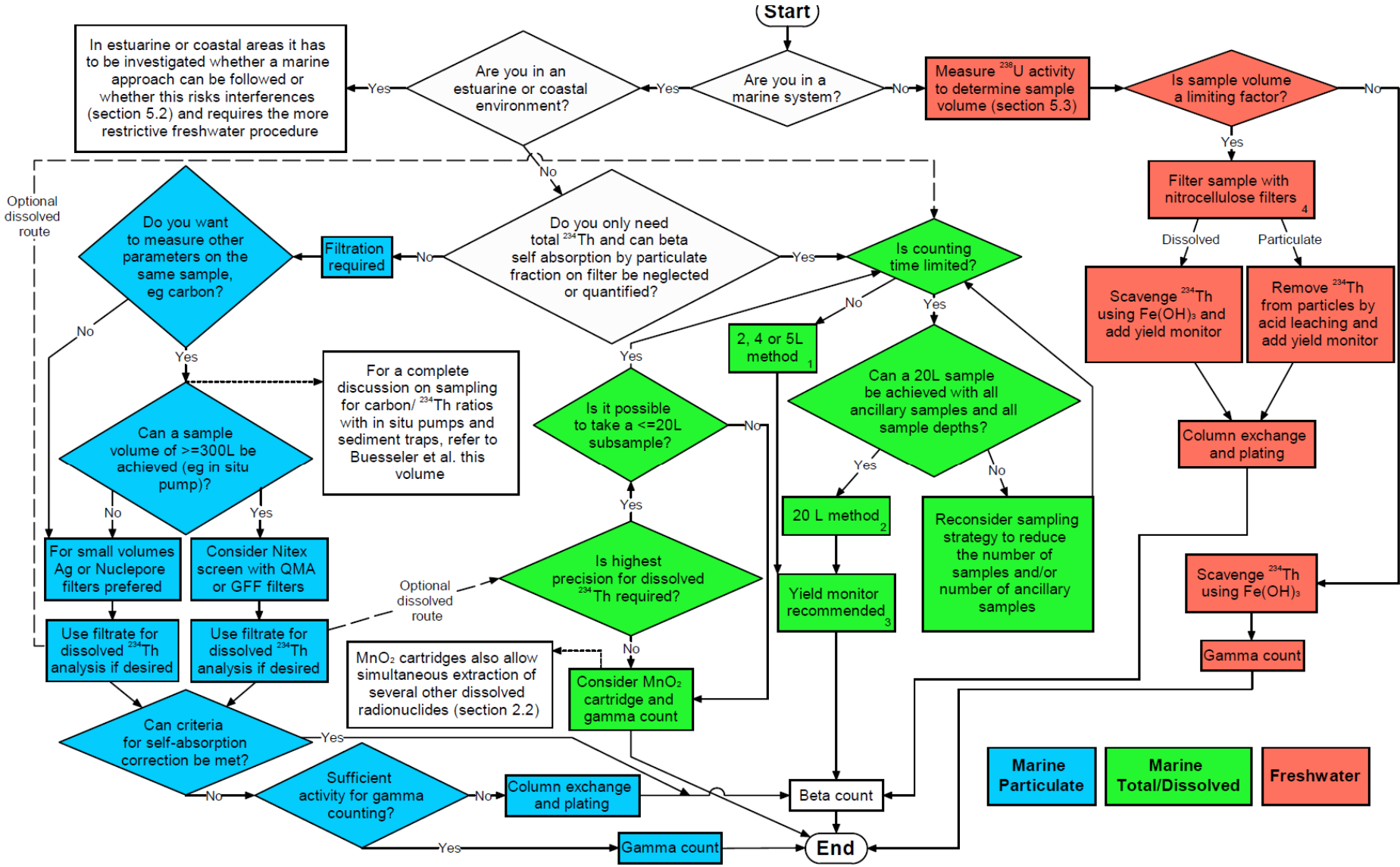
When, where and how to sample ?
An example from the dynamic Øresund area



Roos & Valeur, CSR, 26(4), 474-487, 2006


Continous salinity (ppt)
measurements at 9m depth stn 9
(Nordre Röse)
Salinity (ppt)
35
30
25
20
15
10
5
0
17-Feb
17-Mar
31-Mar
04-May
25-May
29-Jun

Sampling strategy for Th-234 in water



Rain-collector with ion-exchange column

Figure 2.7. Ion-exchange fallout collection and fallout pot collector.

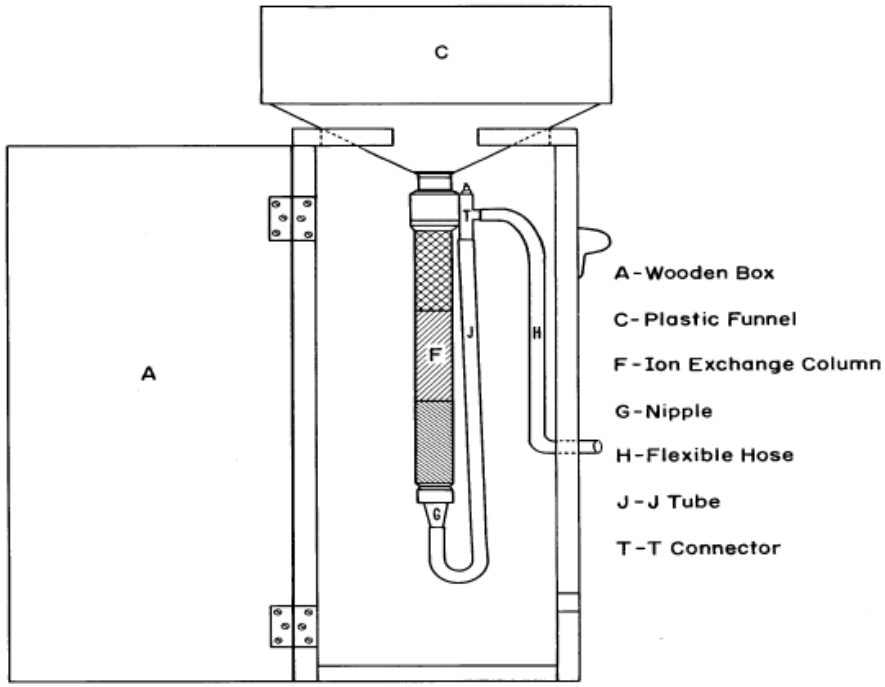
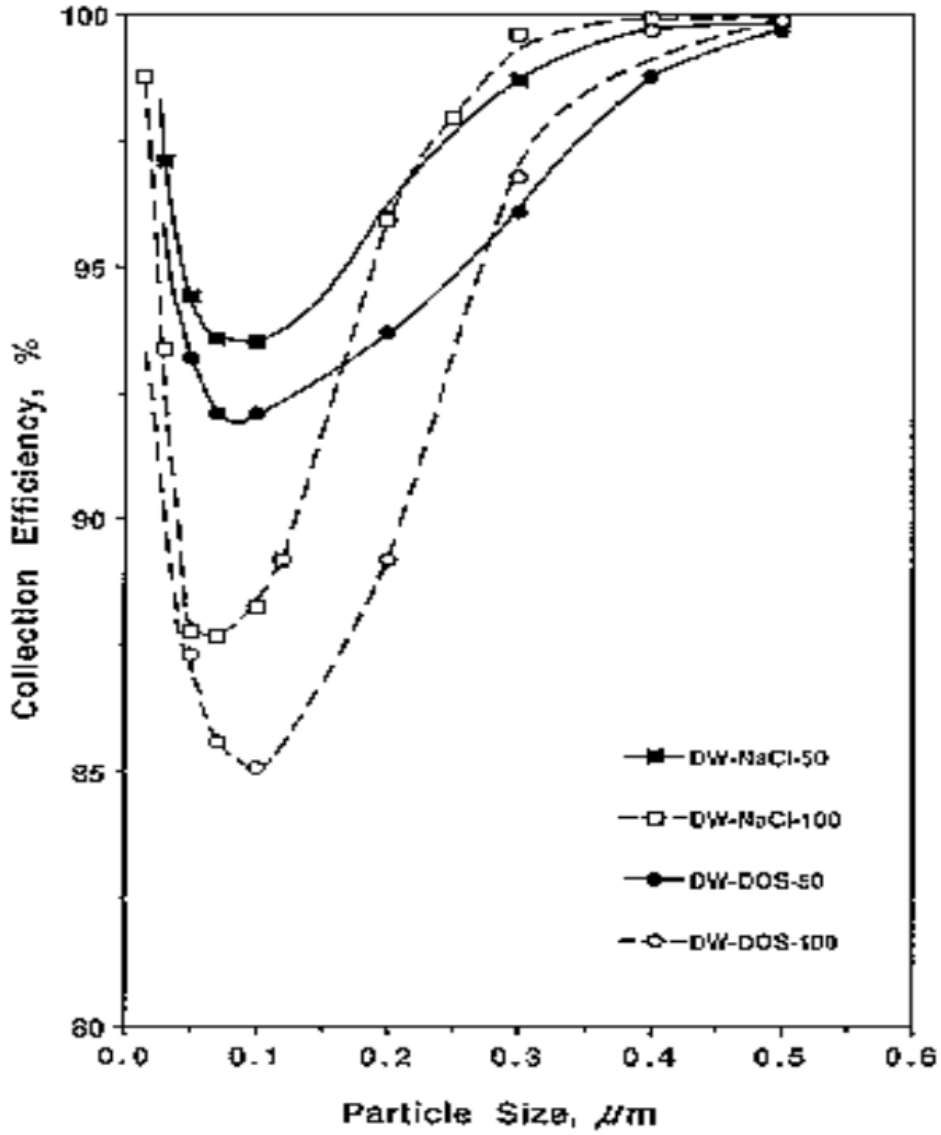


Figure 2.8. Ion-exchange fallout collector.

Wet & dry precipitation

Figure 2.9. Aerochem metrics wet/dry collector and EML wet/dry collector.

Air – incomplete collection of all aerosols



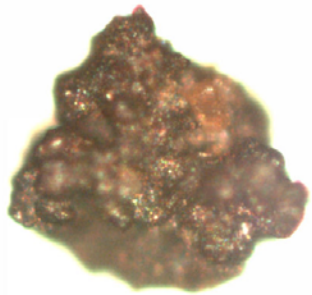
Collection efficiency depends on
- Flow rate
- Total amount of collected material
- Filter type

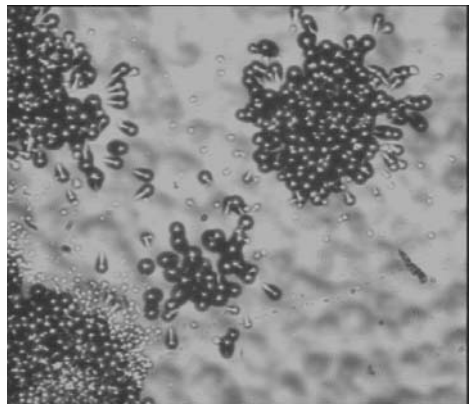

Collecting resuspended soil & aerosols on sticky surfaces

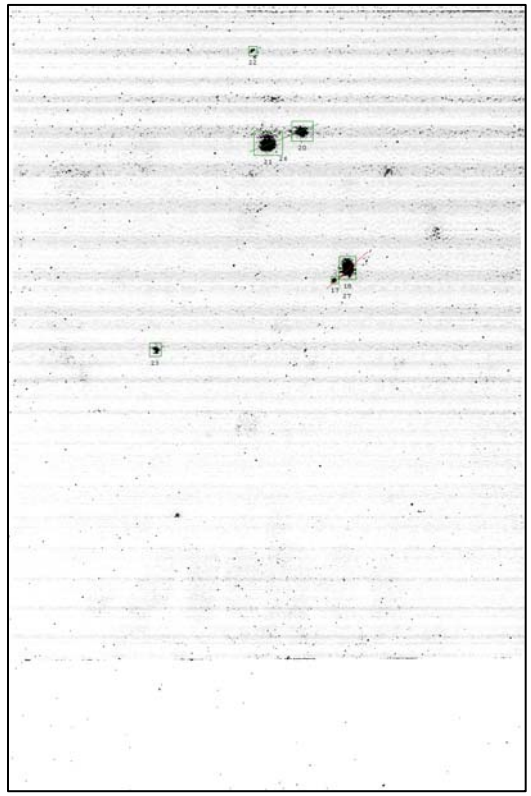

Soil sampling

Radioactive particles

- Digital autoradiography, track-etch detectors and using dry or wet sample splitting using ^{241}Am (59keV gamma).







Techniques for sampling radioisotopes in water

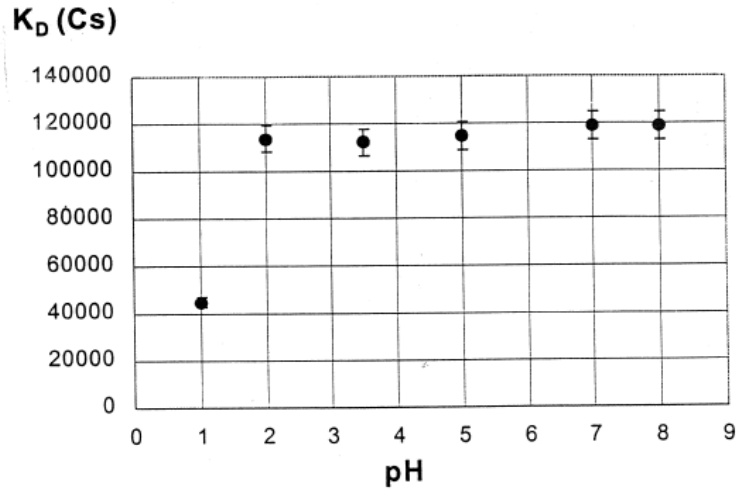
- On site ”bucket chemistry”
- Collecting water and bringing to home laboratory (only total conc !)
- In-situ sampling using sorbents

Adsorbents for direct sampling in water

- Cs – Transition metal ferrocyanides.
- Th & Ra – MnO_2
- Tc – Activated carbon

Radiocesium

- Chloroplatinate (H_2PtCl_6)
- Ammoniummolybdophosphate
- Transition metal ferrocyanides



:

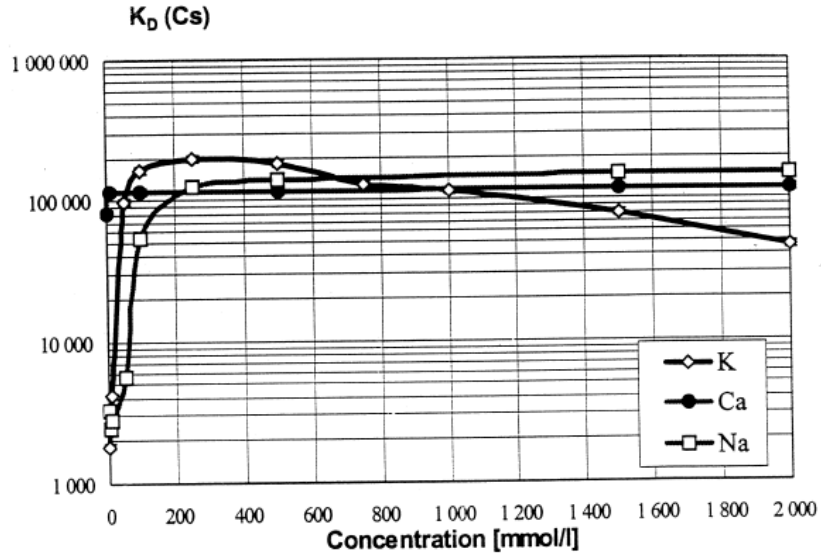
$Fe(CN)_6^{4-} + 2M^{2+} \rightarrow M_2[Fe(CN)_6]$

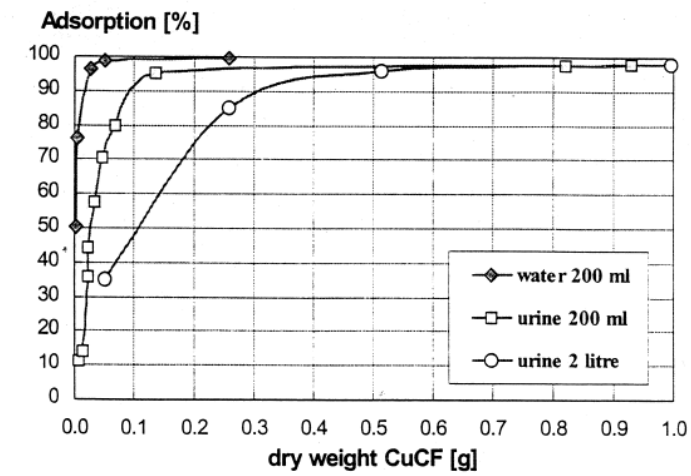
$Cu_2[Fe(CN)_6]$

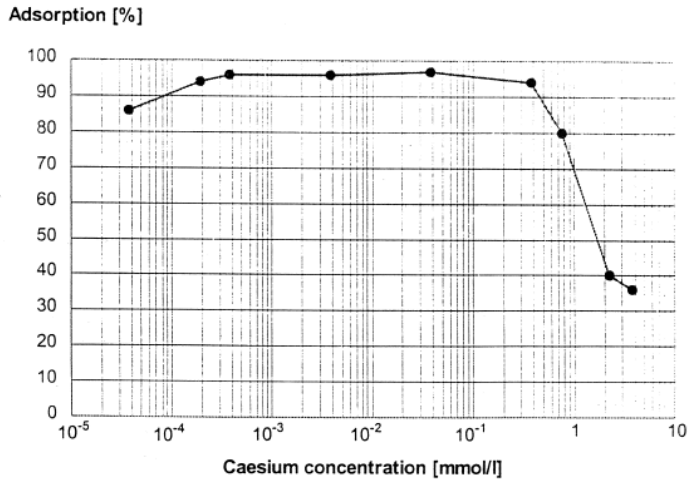
$K_2Cu[Fe(CN)_6]$.

zink and copper ferrocyanide have been reported to have the highest caesium adsorption capacity reaching values of around 1.5 mol/mol for CuFC.

In normal environmental waters the concentrations of stable caesium is in the order of sub-ppb







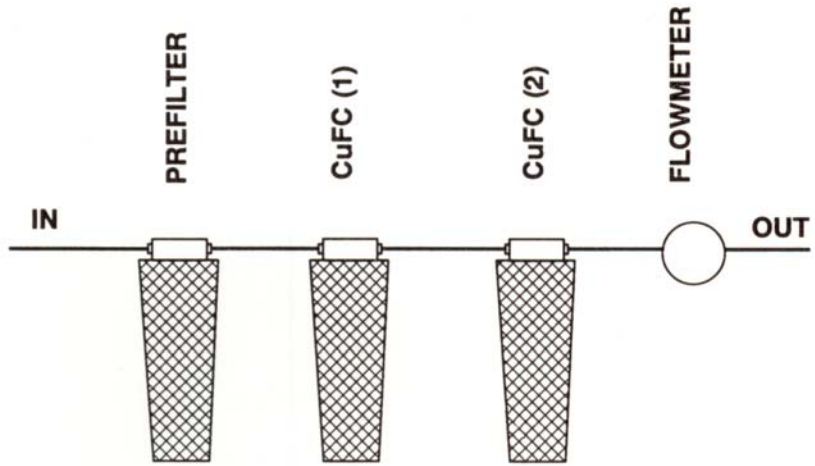


Fig. 1. Large volume in-situ sampling system used for radiocesium. The equipment consists of one prefilter (1 μm), two CuFC impregnated, cotton-wound cartridge filters and a flow meter.

$$\text{Efficiency} = 1 - \frac{\text{CuFC(2)}}{\text{CuFC(1)}}$$

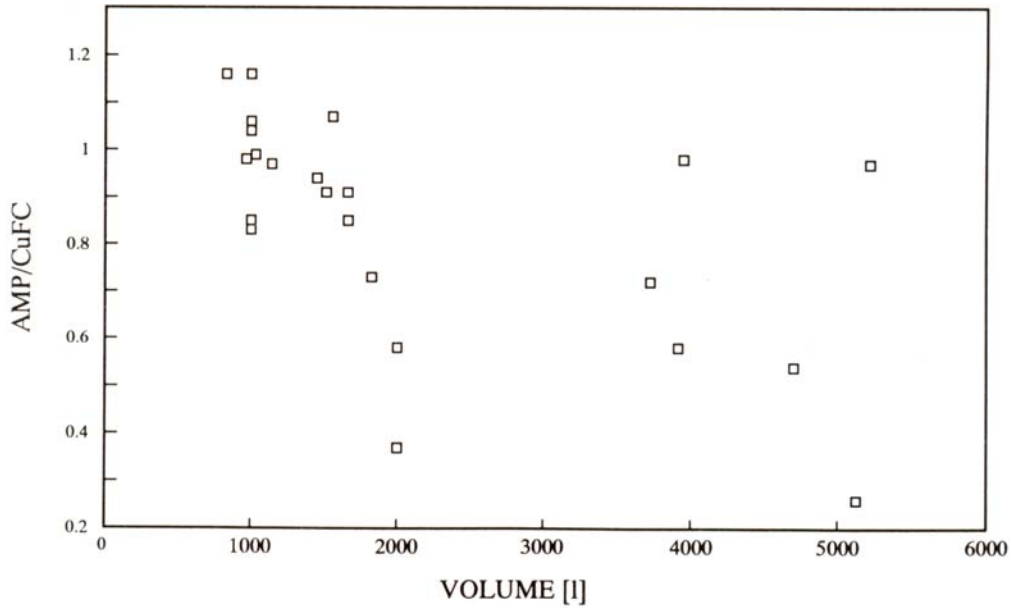


Fig. 2. The AMP/CuFC ratio as a function of filtered water volume for samples collected during the Swedish Antarctic Research

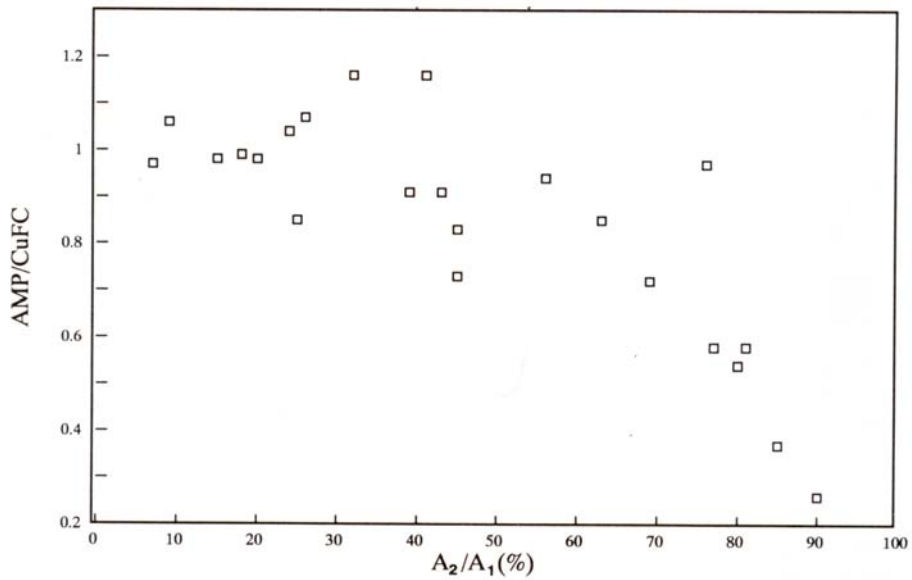


Fig. 3. The AMP/CuFC ratio as a function of ratio of radiocesium on the second and first CuFC filter, A_2/A_1. Samples from the Swedish Antarctic Research Expedition (SWEDARP), 1989.

MnO_2 impregnated fibre (sorption of Ra & Th)

acrylic

polypropylene

In-situ pumps for MnO2 (or any other adsorbent)

MnO_2 impregnated acrylic fibre

Gamma branching ratio:

63 keV
3.8 %

93 keV
5.4 %

Gamma count

Melt/
crush

ash

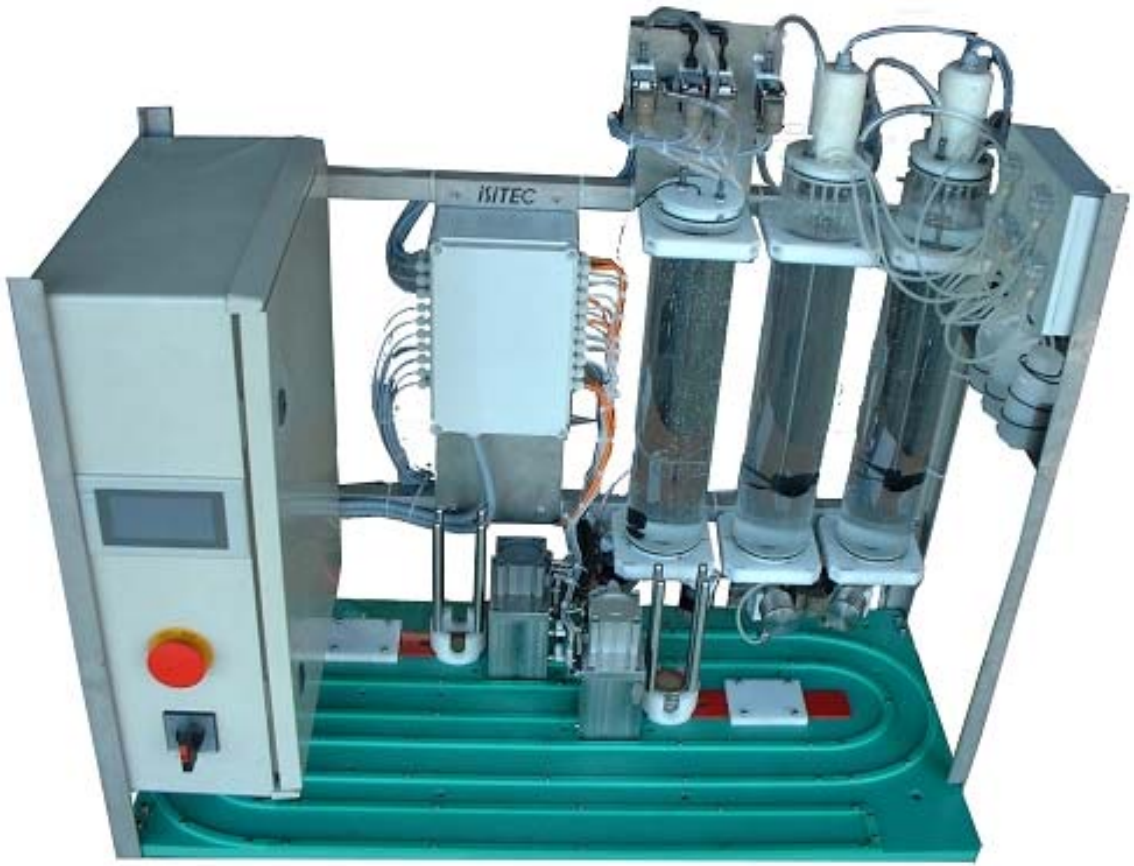
< 1 %

5.3 %

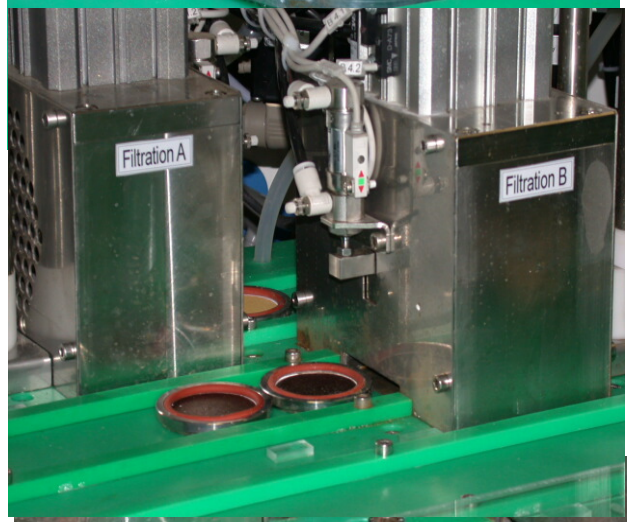
16.1 %

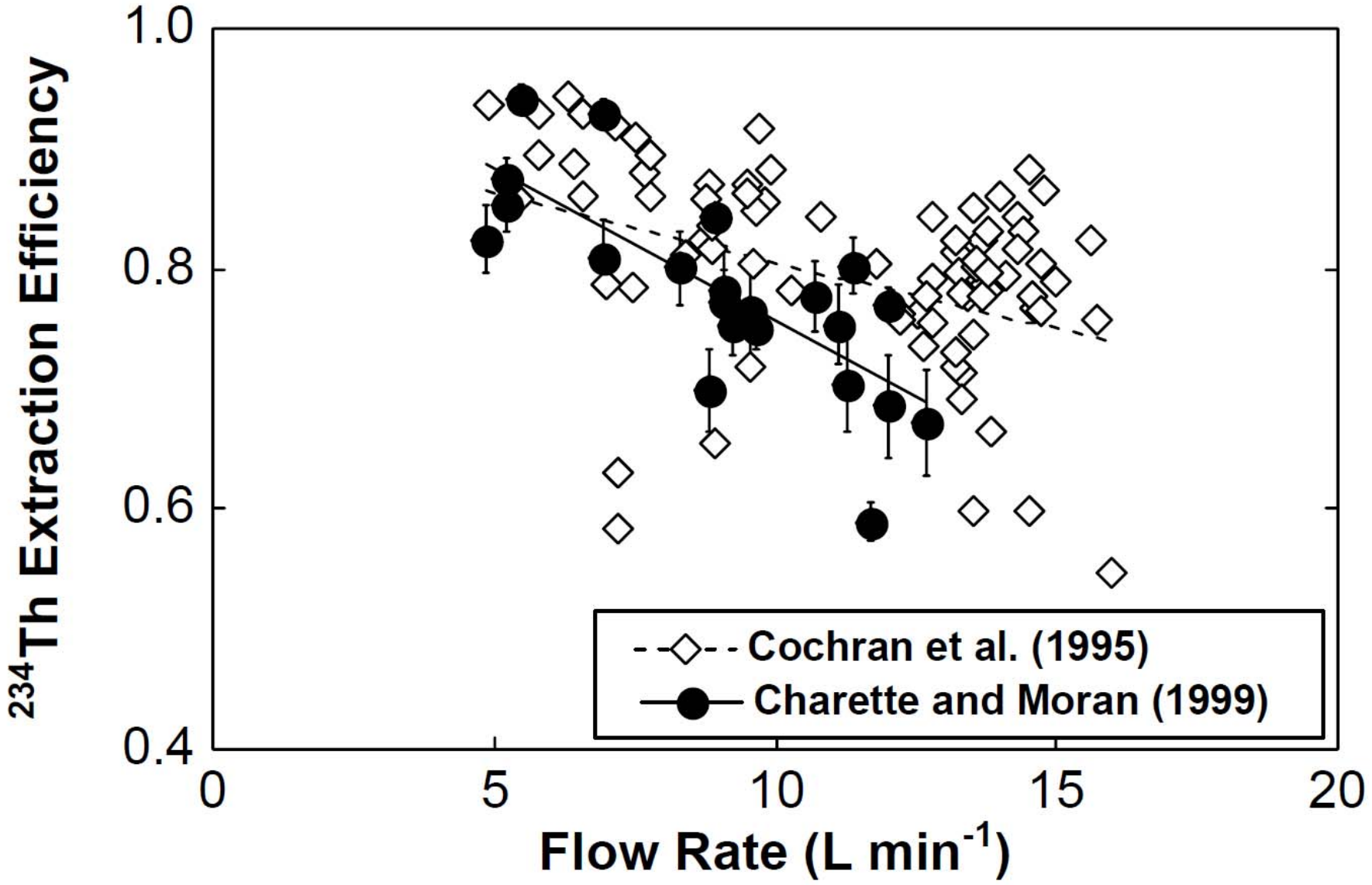
automation

2004

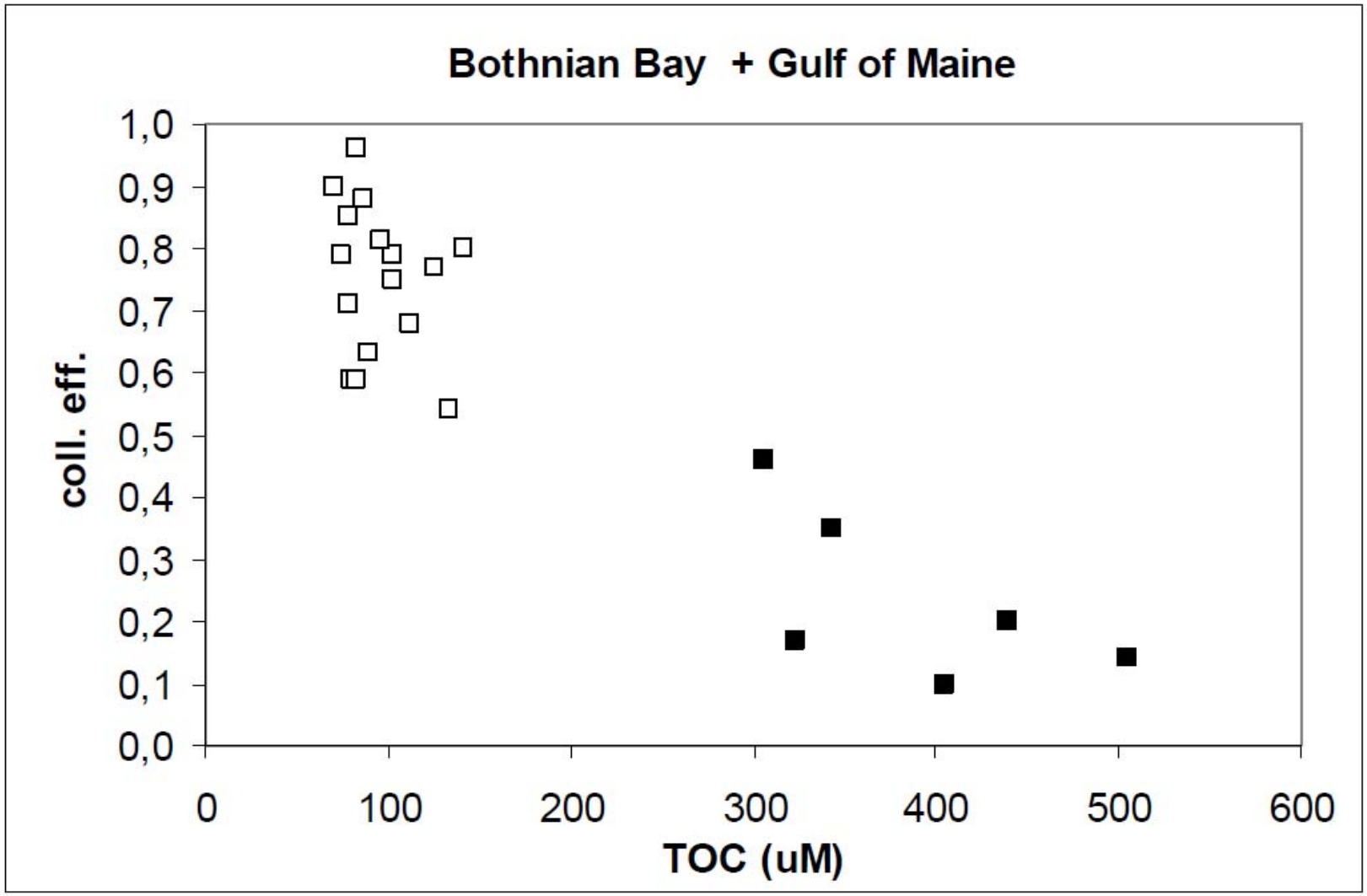


AWI and ISITEC




1.0
0.8
0.6
0.4
0
5
10
15
20
^{234}Th Extraction Efficiency
Flow Rate (L min^{-1})
Cochran et al. (1995)
Charette and Moran (1999)

Uptake of Th & Ra on MnO_2 limited by DOC in water
Volume of filtered water about 500 litres.



Tc-99 adsorption on activated carbon cartridges

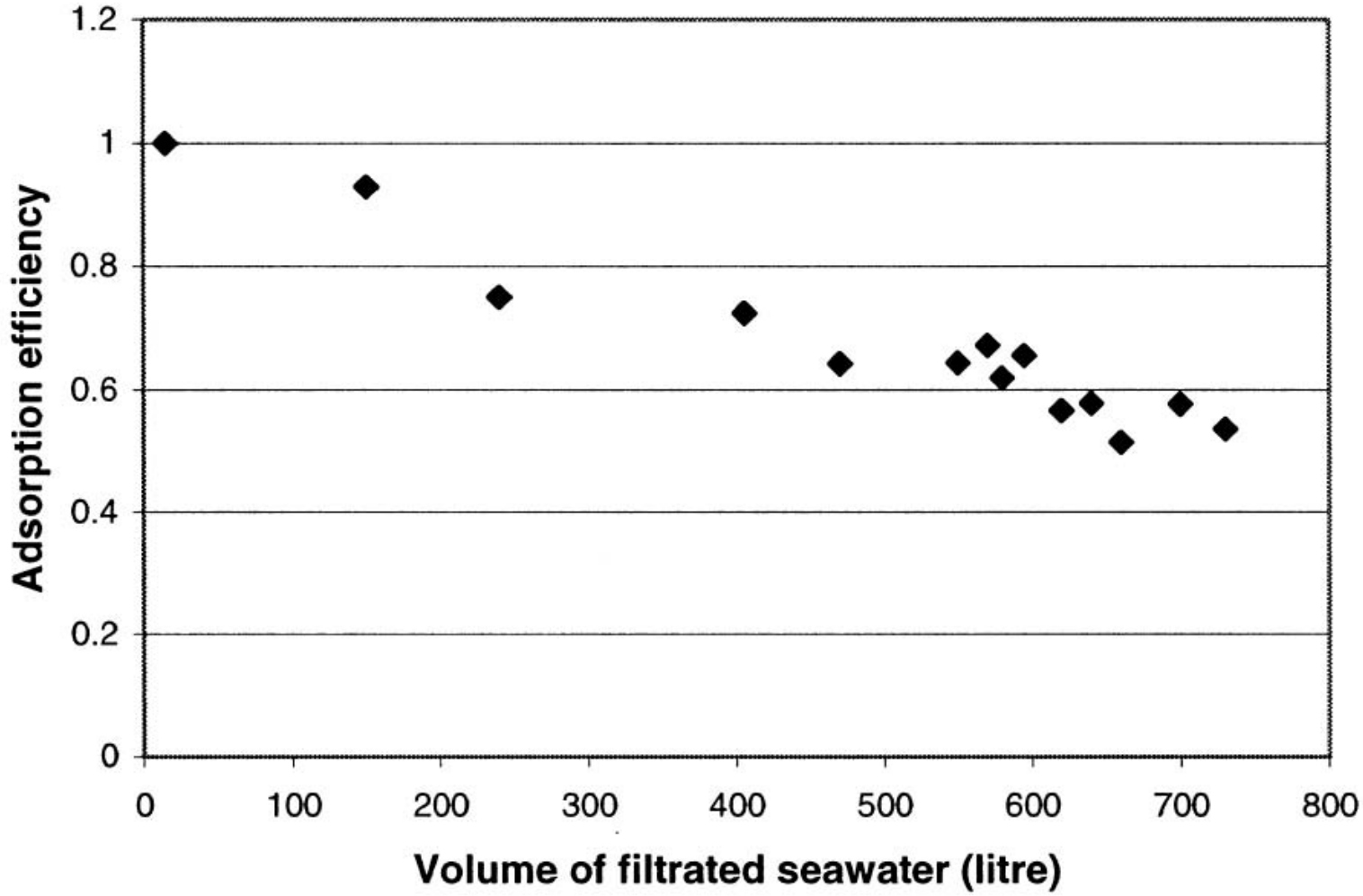
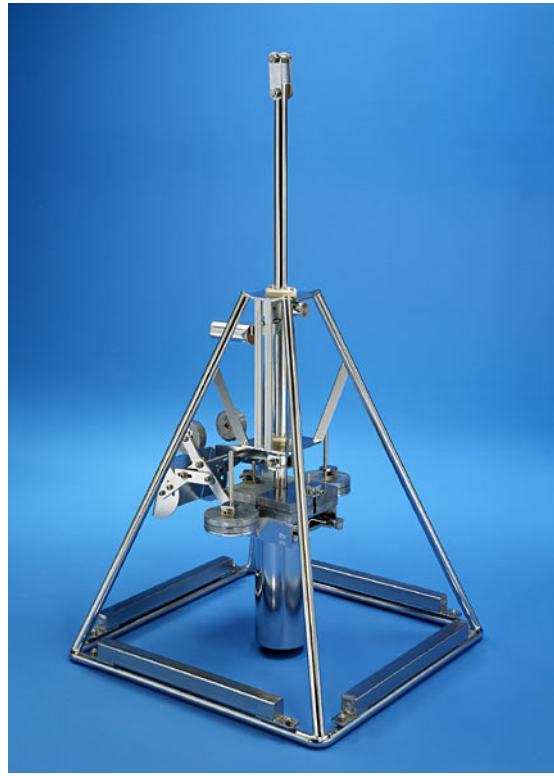
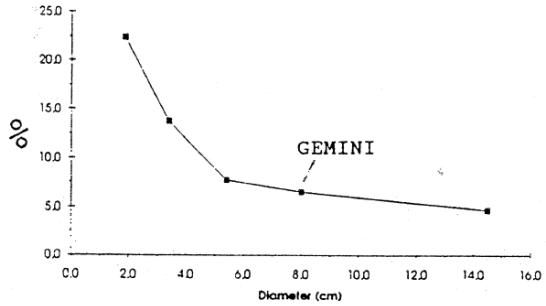


Fig. 3. Adsorption efficiency for Tc from seawater on a cartridge active carbon filter.

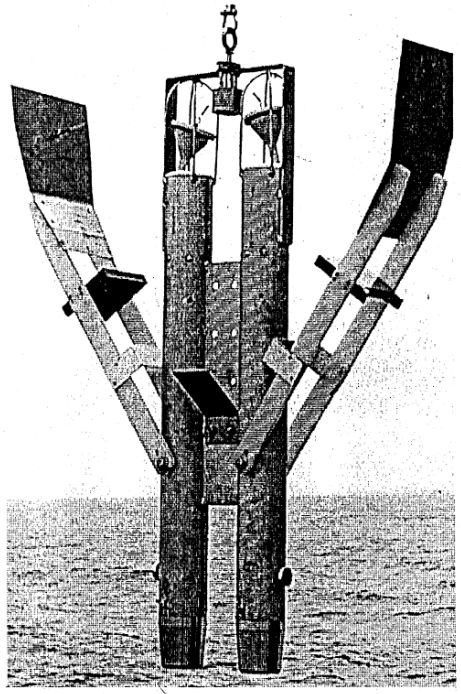
Sediment sampling



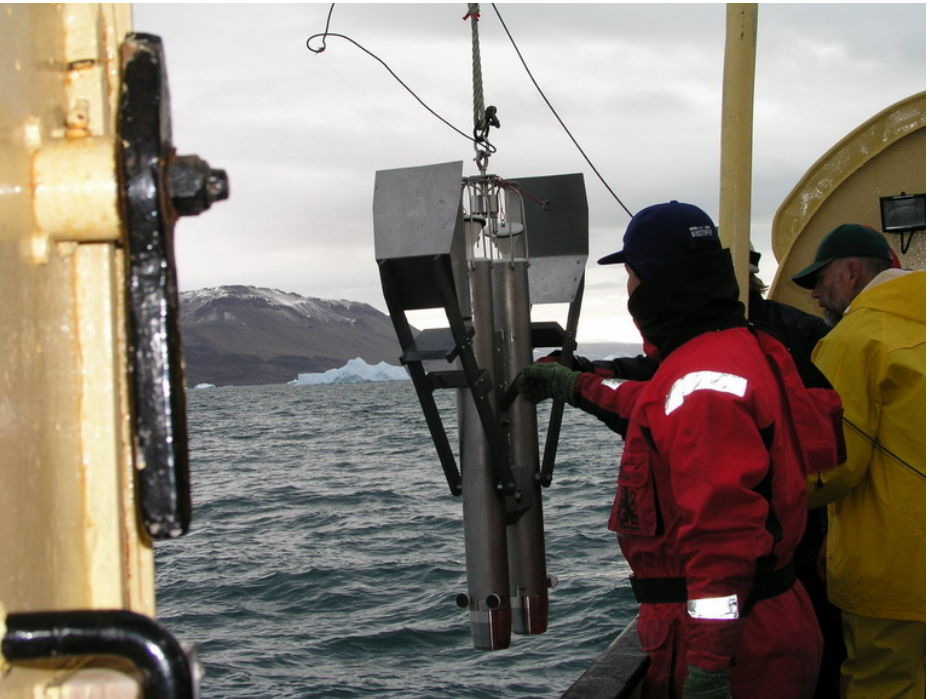
*NIEMISTÖ, L. 1974. A garavity corer for studies of soft sediments. Merentutkimuslait. Julk./Havsfoskningsinst. Skr. 238:33-38.

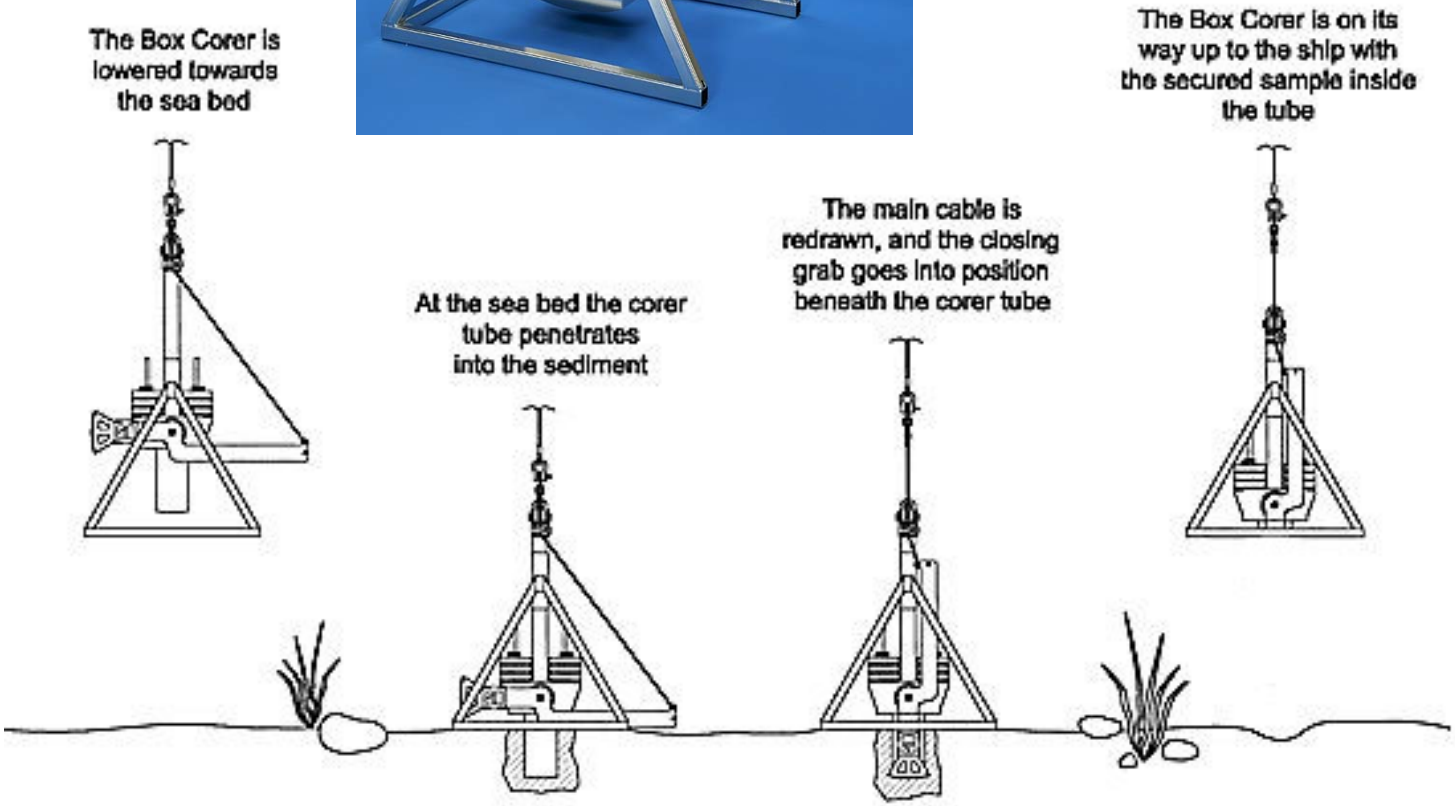


Core shortening (%) as a function of corer diameter (cm).
From: Blomqvist,S. 1985. Reliability of core sampling of soft bottom sediment - an *in situ* study. Sedimentology (1985) 32, 605 - 612.



"Gemini" ready to descend. The two rudders and the valves are fixed with nylonstrings and keep this position until bottom touch. A slight slack of the wire opens the pins and the rudders and valves are free to close.




The Box Corer is lowered towards the sea bed
At the sea bed the corer tube penetrates into the sediment
The main cable is redrawn, and the closing grab goes into position beneath the corer tube
The Box Corer is on its way up to the ship with the secured sample inside the tube

Freeze-coring

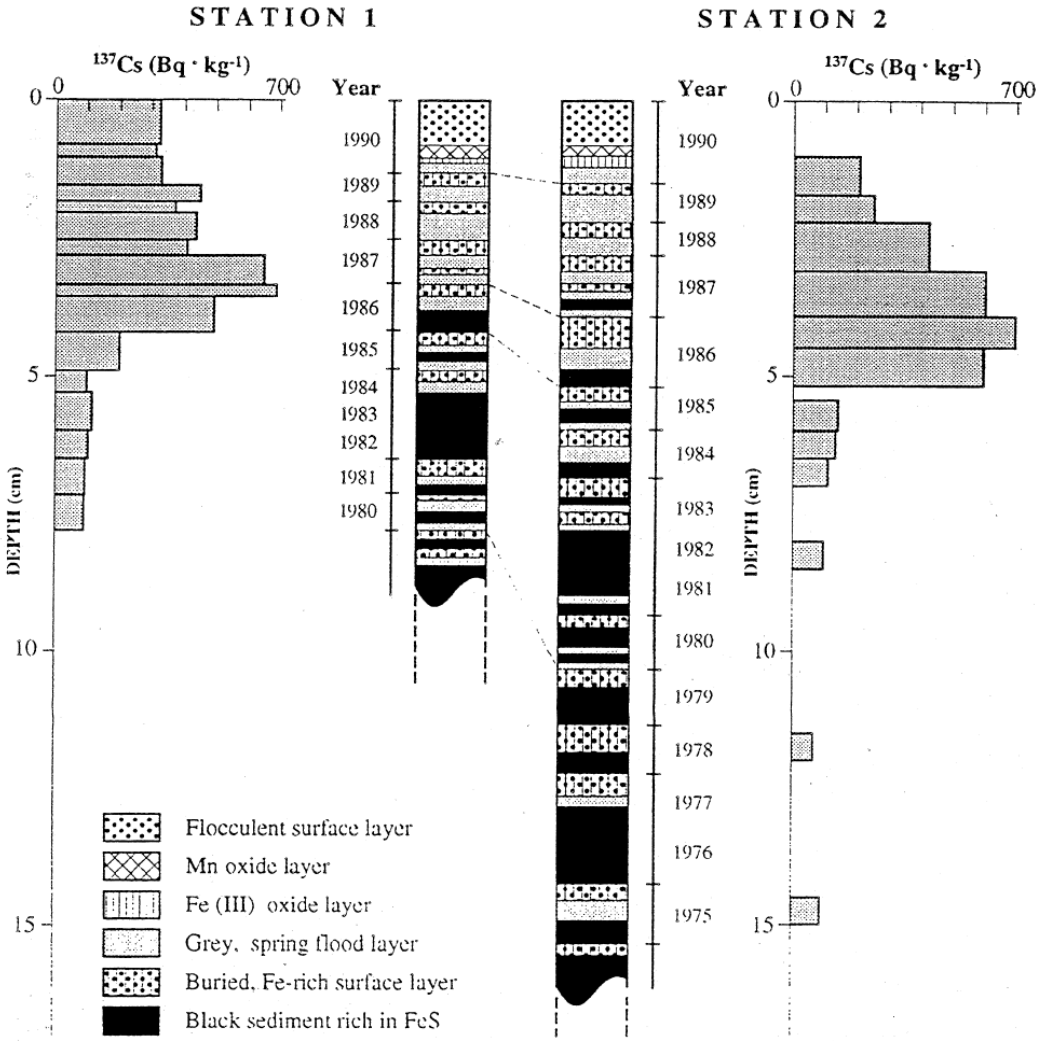
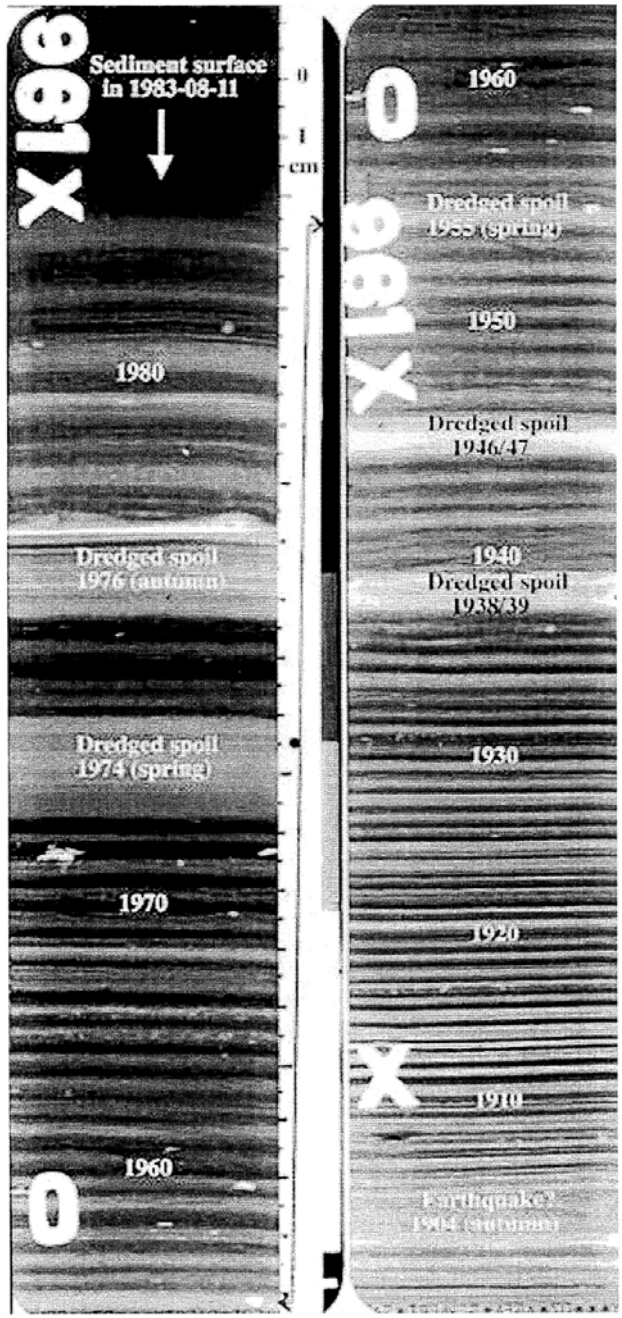
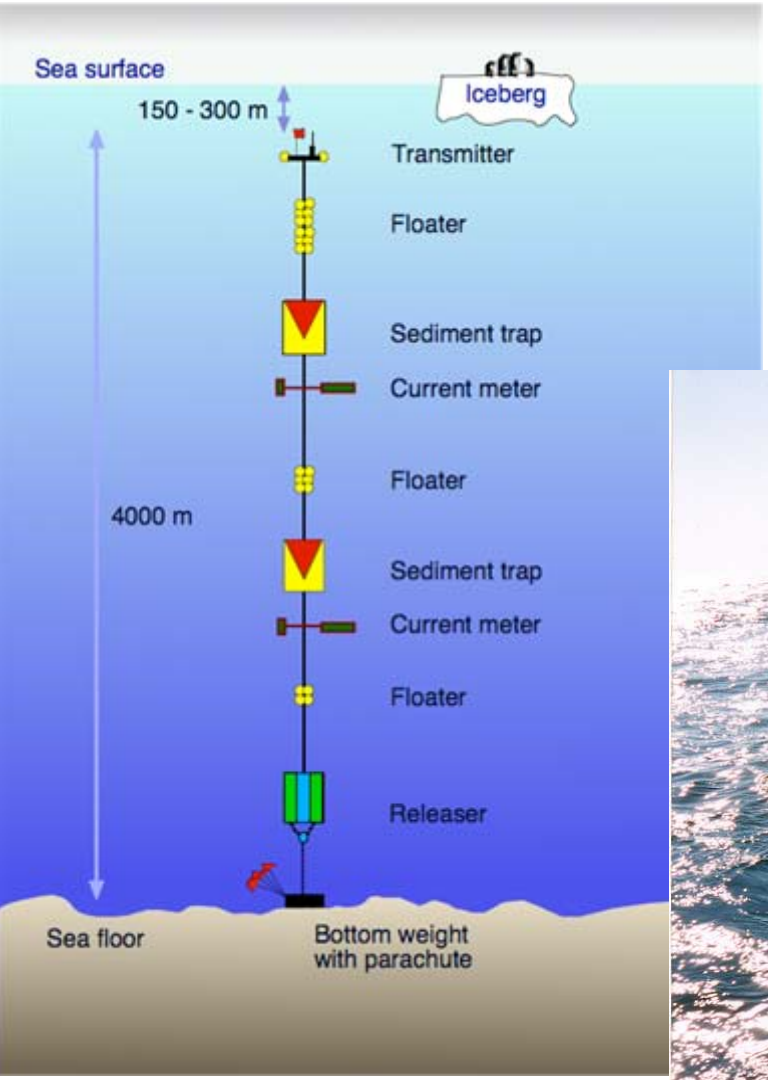


Fig. 2. ^{137}Cs in selected sediment sections and varve-counts for the two cores investigated. Fall-out from the Chernobyl accident resulted in a 7–10 fold increase of ^{137}Cs in the Fe-rich layer deposited during the summer and autumn of 1986. A tentative correlation of individual varves between the two stations is indicated.



Benthic landers

Sediment traps and water samplers



Samplers for speciation studies (chemical form, size etc)

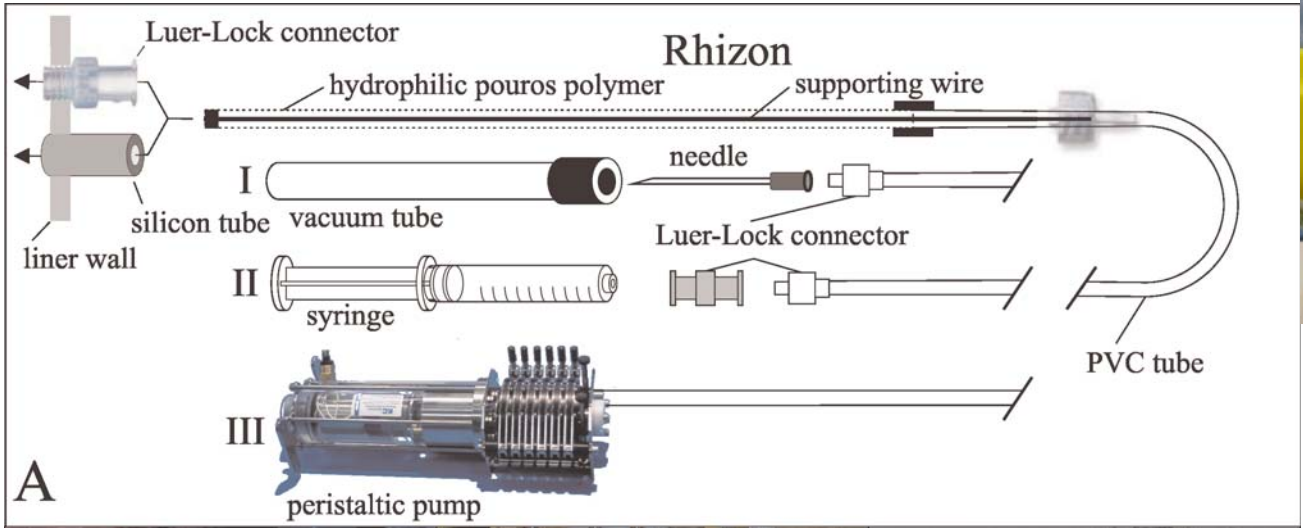
Sediment & soil interstitial water

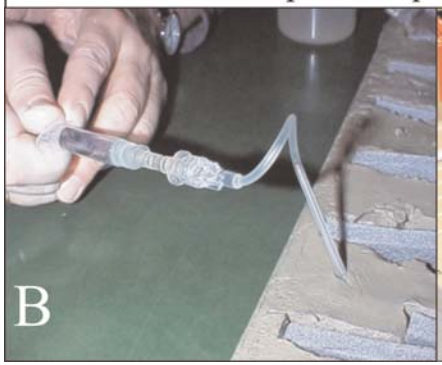
- Centrifugation and filtering of soil or sediment interstitial water. Nitrogen flushing.
- Porous cups (with vacuum).
- Rhizon-samplers (artificial porous ’roots’).
- Diffusive Gradient in Thin film samplers (DGT-samplers).

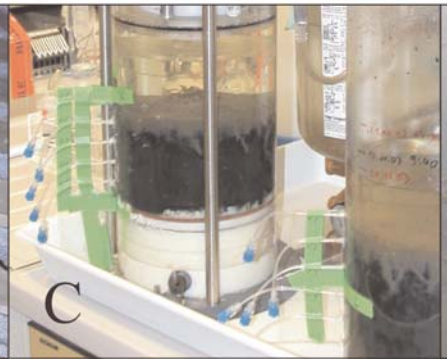
Water

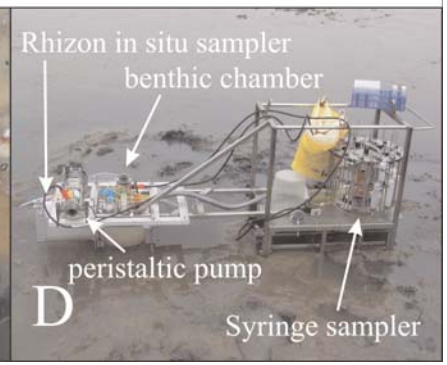
- Filtration & ultra-filtration.
- Selected co-precipitation techniques.
- Field Flow Fractionation (FFF)

Rhizon-samplers

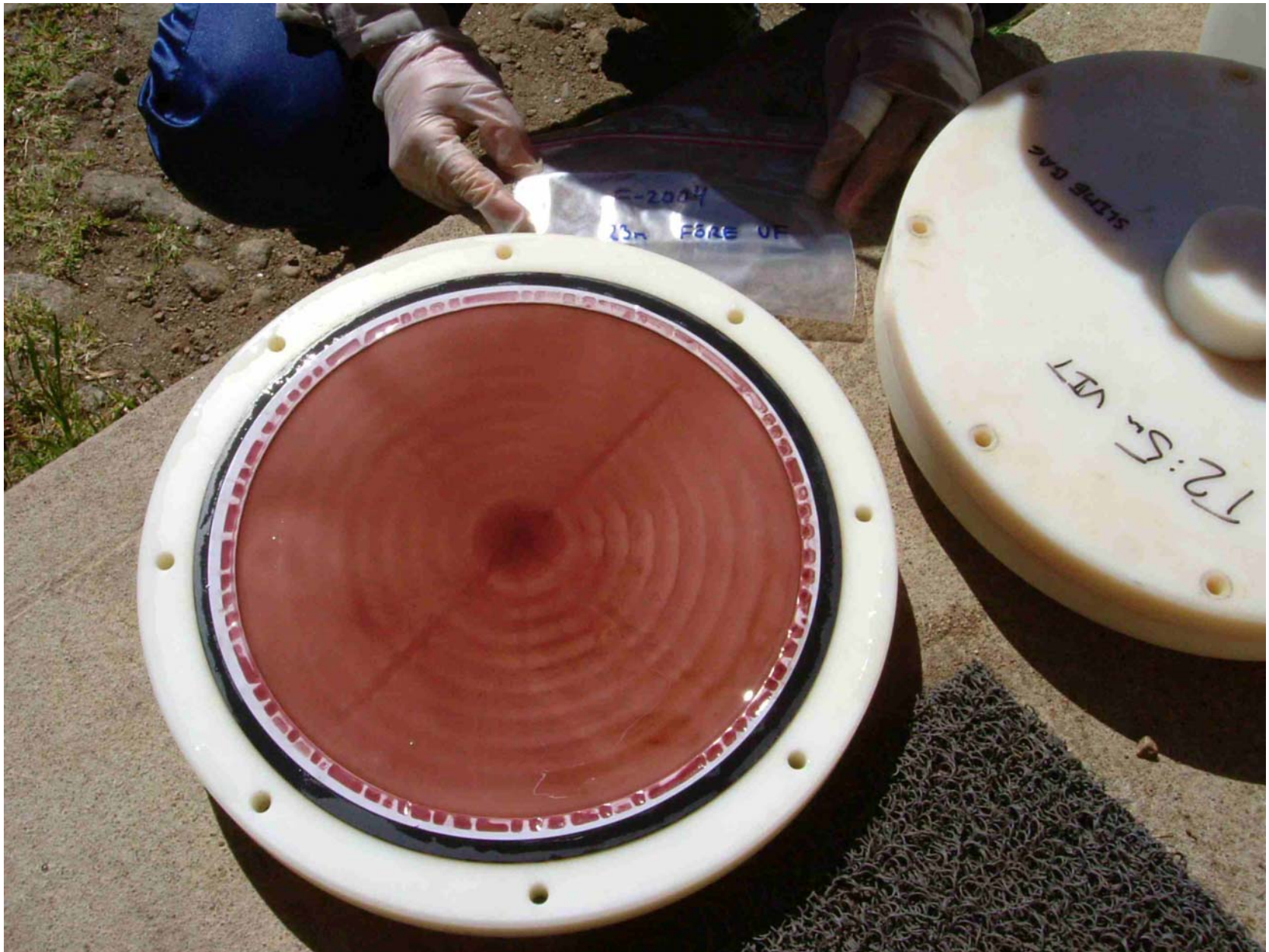




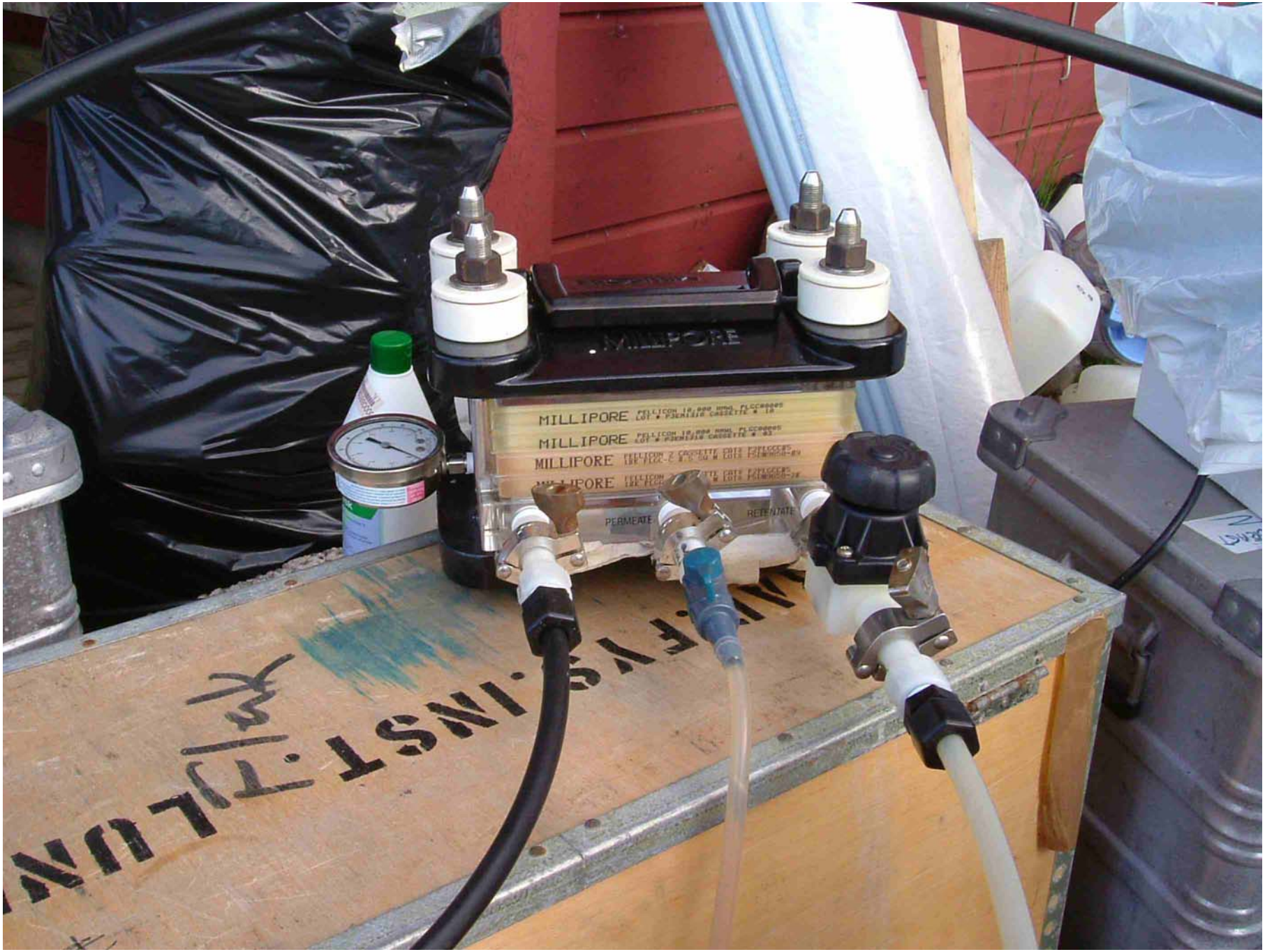




Filtration 0.45 µm with 293mm diameter membrane



Cross-flow large volume ultrafiltration


MILLIPORE
MILLIPORE
MILLIPORE
MILLIPORE
PERMEATE
RETENTATE

Ultrafiltration with permeate and retentate fraction

In-situ filtration & ultrafiltration

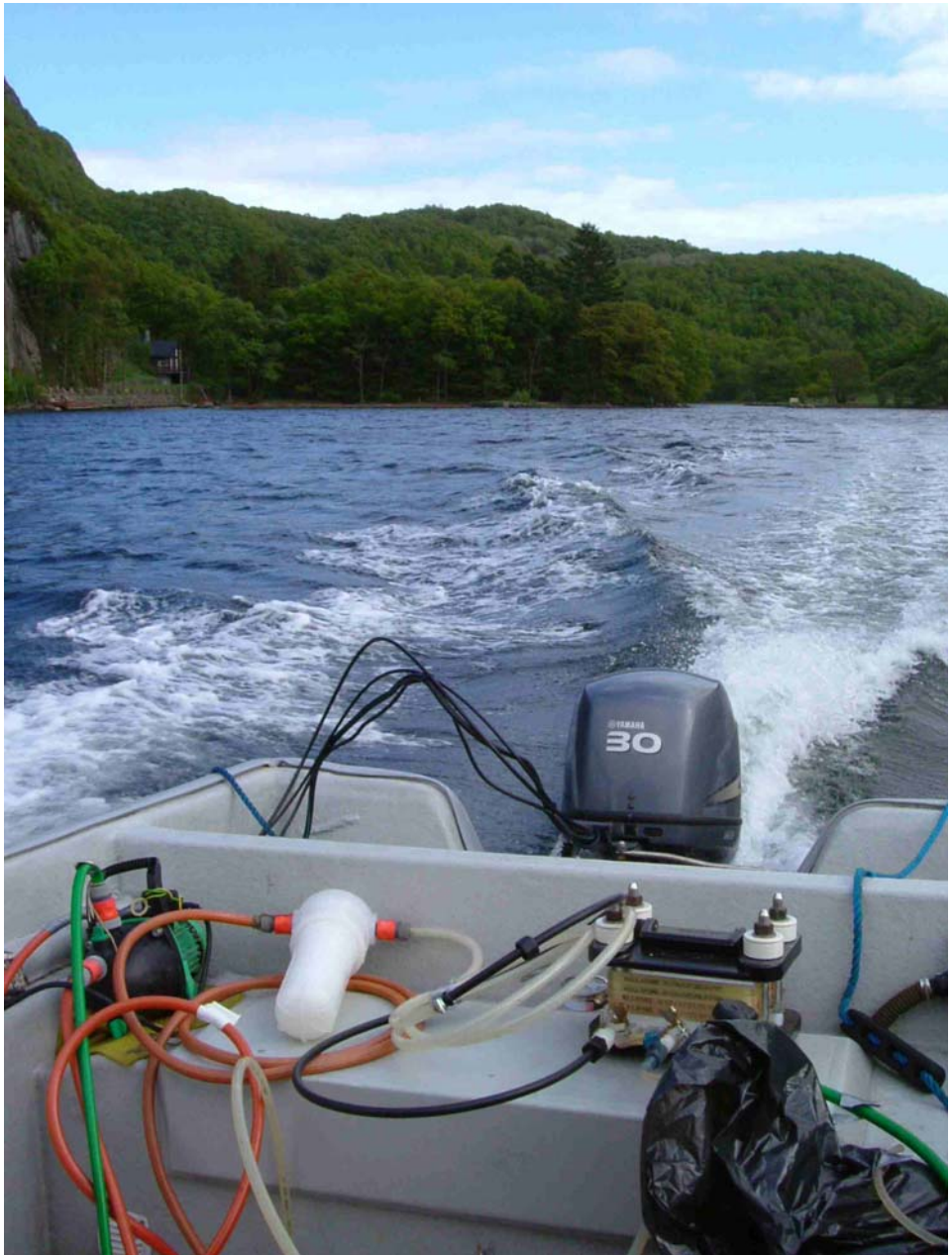
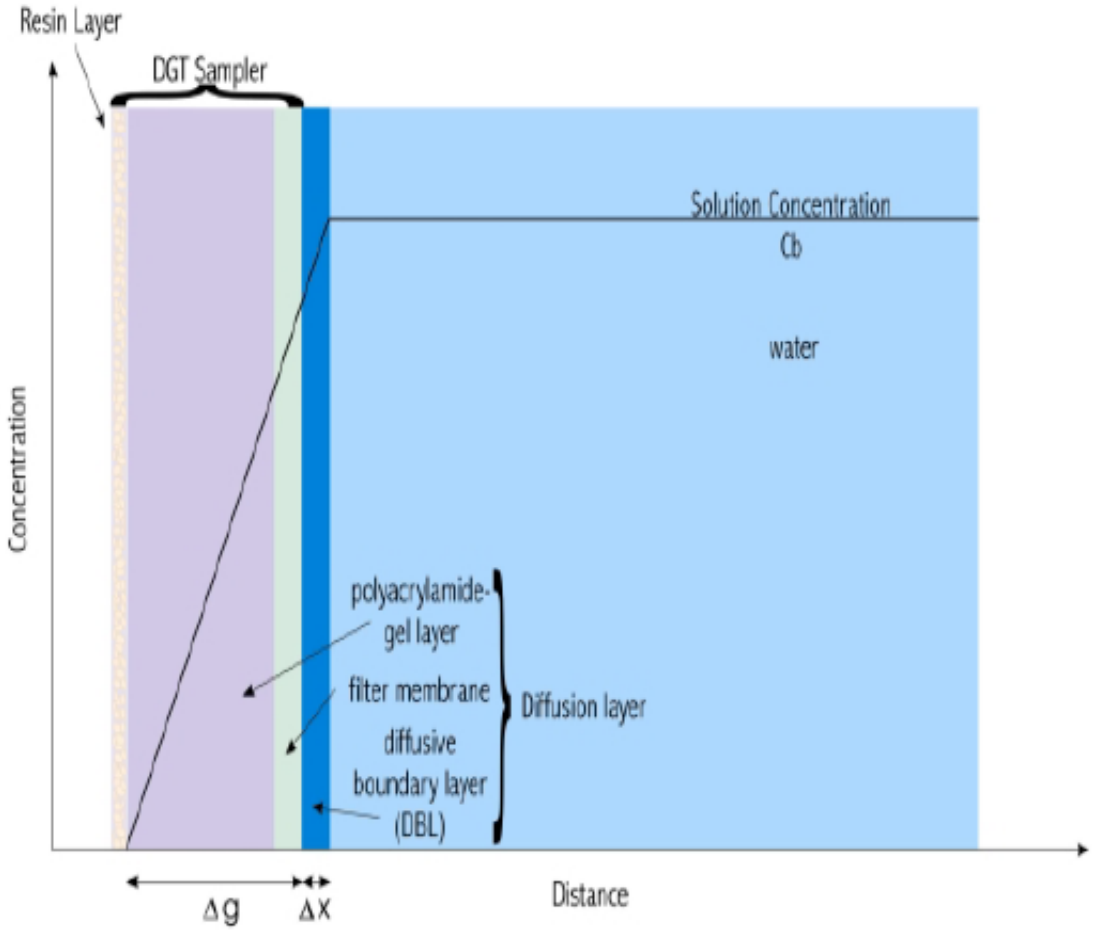


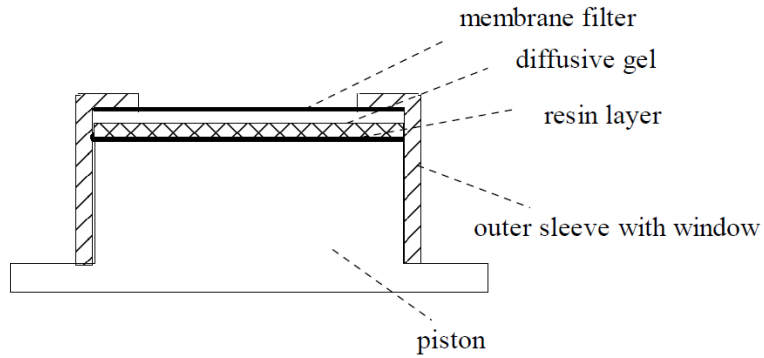
TABLE 10.1—Summary of sample preservation techniques.

Preservation Technique	Advantages	Disadvantages
Addition of HNO_3	Reduces pH and inhibits plating of metals on container walls.	Strong oxidizer that might react with organic compounds, such as liquid scintillation cocktails. ^{14}C might be lost as $^{14}CO_2$.
Addition of HCl	Reduces pH and inhibits plating of metals on container walls. Chloride forms strong anionic complexes with Iron and Uranium.	Causes quench in liquid scintillation cocktails. ^{14}C might be lost as $^{14}CO_2$. Might cause corrosion of stainless steel planchets on gross analyses.
Addition of Sulfite	Forms a reducing environment to prevent the volatilization of iodine.	May produce undesirable oxidation states of iron or uranium.
Addition of Formaldehyde	Preserves organic samples. Prevents further biological activity.	May create disposal problems.
Cooling (Ice at approximately 0 °C)	Preserves organic samples (i.e., water, foods). Reduces dehydration and retains moisture. Reduces biological activity.	Ice melts, requiring replacement over time.
Freezing (Dry Ice at approximately -78 °C)	Preserves organic samples (i.e., water, plant, animal). Suspends biological activity.	Dry ice sublimates and requires replacement. May crack sample container if frozen too quickly.
Addition of Paper Pulp	Provides large surface area for adsorption of metals, thus minimizing adsorption on container walls.	Requires pH to be one or less. Requires filtration and wet ashing of paper pulp and combining liquids to make a new solution.

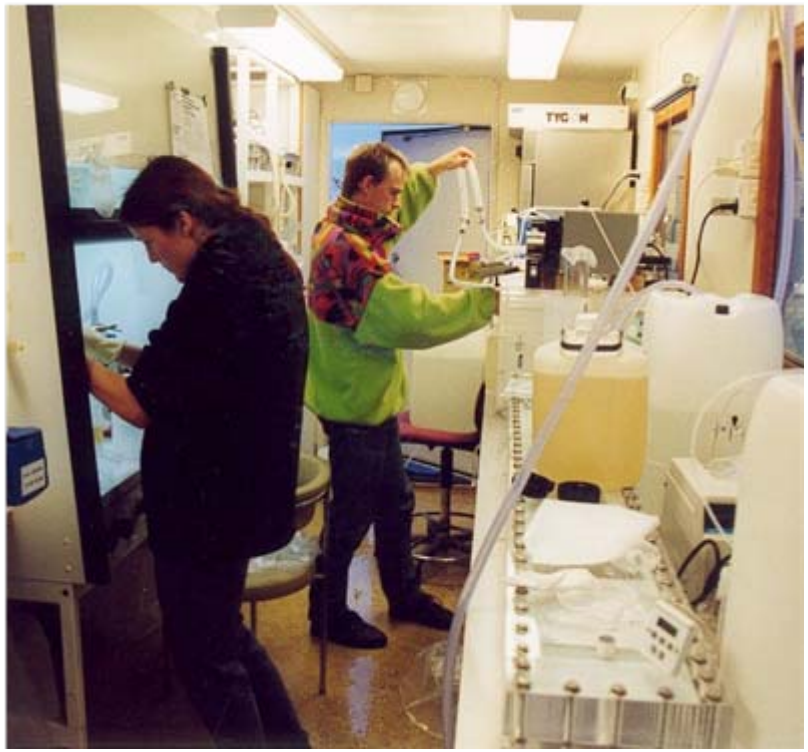
DGT-samplers



$$Q = \frac{gD \cdot A \cdot t}{\Delta g} \cdot C_b$$



Ship-based Field Flow Fractionation system



Sample treatment

- Pre-treatment involving drying, sieving, ashing, filtering and precipitation
- Chemical preparation, purification and isolation of the elements in question

Measurement methods & radiochemistry

	Chemical analysis	Liquid scintillation counting	Gamma spectrometry	Total beta counting	Alpha spectrometry	ICPMS	Neutron activation analysis
^{3}H	X	X					
^{90}Sr	X	X		X			
^{99}Tc	X			X		X	
^{129}I	X						X
^{137}Cs	X		X				
^{210}Pb			X				
^{210}Po	X				X		
^{226}Ra	X	X	X				
^{230}Th	X				X		
^{232}Th	X				X	X	
^{234}U	X				X	X	
^{238}U	X				X	X	
^{237}Np	X				X	X	
^{239}Pu	X					X	
^{240}Pu	X					X	
$^{239+240}Pu$	X	X			X		
^{241}Am	X				X		
Other gamma emitters			X				

Decomposition metods

- **<u>Dry oxidation</u>** -550-600 ^{0}C. Too high temperature-volatile elements, oxides difficult to dissolve.
- Use of ashing acids, HNO_3, H_2SO_4, oxalic acid

TABLE 12.3 — Examples of dry-ashing temperatures (platinum container)

Element	Temperature/Matrix
Cobalt	450–600 °C for biological material; some losses reported due to reactions with crucible; increased volume of sample increases volume of ash and limits loss of sample.
Cesium	400–450 °C for food and biological material; CsCl and $CsNO_3$ begin to volatilize when held at temperatures above 500 °C for any length of time.
Iodine	450–500 °C with an alkaline ashing aid to prevent volatilization; losses reported for temperatures as low as 450 °C even with alkaline ashing aids added; total volatilization >600 °C.
Lead	450–500 °C acceptable for most samples; bone or coal (lead phosphate) may be ashed as high as 900 °C without significant losses; PbO_2 reacts with silica in porcelain glaze at low temperatures; $PbCl_2$ is relatively volatile and nitrate or sulfate ashing aids have been used to good effect.
Plutonium	450 °C with nitric acid ashing aid for biological material, 550 °C for dust on air filters, 700 °C for soil; high temperature leads to adsorption onto carbon particles and incomplete dissolution of ash.
Strontium	450–550 °C for plants, 600 °C for meat, 700 °C for milk and bone.
Technetium	725–750 °C for plants treated with ammonia.
Thorium	750 °C for bone.
Uranium	600 °C for coal, 750 °C for biological material; uranium reacts with porcelain glaze resulting in sample losses.

Source: Bock (1979).
(Note that reducing conditions for platinum containers are given in Table 12.2)

TABLE 12.1 — Examples of volatile radionuclides

Isotope	Chemical Form	Boiling Point (°C) *
Tritium — ^{3}H	H_2O	100°
Carbon — ^{14}C	CO_2 (produced from CO_3^{-2} or oxidation of organic material)	-78.5°
	Magnesium, calcium, and sodium carbonates	Natural ores of these metals decompose between 825° and 1,330° to yield the respective metal oxides
Iodine — ^{131}I, ^{129}I	I_2	185.2° (sublimes readily)
Cesium — ^{134}Cs, ^{135}Cs, ^{136}Cs, ^{137}Cs	Cs^0 (as metal) Cs_2O (as metallic oxide) (nitrates decompose to oxides) CsCl (as metallic chloride)	678.4° (melts at 28) ~400° 1290°
Technetium — ^{99}Tc	Tc_2O_7 $TcCl_4$ TcO_2	310.6° Sublimes above 300° Sublimes above 900°
	[Most Tc compounds sublime above 300°. Tc(VII) is an oxidant that reacts with organic solvents forming Tc(IV)]	
Polonium — ^{208}Po, ^{209}Po, ^{210}Po	Po^0 $PoCl_4$ $Po(NO_3)_4$ [as a solid] PoO_2	962° 390° Decomposes to PoO_2 above ~150° Decomposes to Po metal above 500°
Lead — ^{210}Pb, ^{212}Pb, ^{205}Pb	Pb^0 $PbCl_2$ $Pb(NO_3)_2$ PbO	1744° 950° Decomposes to oxide above 470° 888°

* The closer the sample preparation temperature is to the boiling point of the compound, the more significant will be the loss of the material. However, if the objective is to distill the analyte compound from other nonvolatile materials, then boiling temperature is needed. Sample preparation near the decomposition temperature should be avoided for those compounds that have a decomposition temperature listed in the table.

Sources: Greenwood and Earnshaw (1984); Windholz (1976); Schwochau (2000); Sneed and Brasted (1958).

Wet oxidation systems

- HNO_3-$HClO_4$ –danger of explosions
- HNO_3-H_2SO_4
- HNO_3-HCl-H_2O_2
- The last two ones are safer but do not decopose all organic compounds
- **Oxidative fusion**
- For minerals, sediment, fiber glass filters
- Na_2O_2, NaOH, $KHSO_4$, $K_2S_2O_7$
- Often very violent reactions

Wet oxidation

- **-Advantages:**
- lower temperture
- improves isotopic exchange
- low pH, H+ ions fill vacancies in wall containers
- **Disadvantages**
- formation of compounds difficult to dissolve
- background from radionuclides in acids and containers

TABLE 13.2 — Examples of acids used for wet ashing

Acid	Typical Uses
Hydrofluoric Acid, HF	Removal of silicon and destruction of silicates; dissolves oxides of Nb, Ta, Ti, and Zr, and Nb, and Ta ores.
Hydrochloric Acid, HCl	Dissolves many carbonates, oxides, hydroxides, phosphates, borates, and sulfides; dissolves cement.
Hydrobromic Acid, HBr	Distillation of bromides (e.g., As, Sb, Sn, Se).
Hydroiodic Acid, HI	Effective reducing agent; dissolves Sn^{+4} oxide and Hg^{+2} sulfide.
Sulfuric Acid, H_2SO_4	Dissolves oxides, hydroxides, carbonates, and various sulfide ores; hot concentrated acid will oxidize most organic compounds.
Phosphoric Acid, H_3PO_4	Dissolves Al_2O_3, chrome ores, iron oxide ores, and slag.
Nitric Acid, HNO_3	Oxidizes many metals and alloys to soluble nitrates; organic material oxidized slowly.
Perchloric Acid, $HClO_4$	Extremely strong oxidizer; reacts violently or explosively to oxidize organic compounds; attacks nearly all metals.

TABLE 13.1 — Common fusion fluxes

Flux (mp, °C)	Fusion Temperature, °C	Type of Crucible	Types of Sample Decomposed
$Na_2S_2O_7$ (403°) or $K_2S_2O_7$ (419°)	Up to red heat	Pt, quartz, porcelain	For insoluble oxides and oxide-containing samples, particularly those of Al, Be, Ta, Ti, Zr, Pu, and the rare earths.
NaOH (321°) or KOH (404°)	450-600°	Ni, Ag, glassy carbon	For silicates, oxides, phosphates, and fluorides.
Na_2CO_3 (853) or K_2CO_3 (903)	900-1,000°	Ni Pt for short periods (use lid)	For silicates and silica-containing samples (clays, minerals, rocks, glasses), refractory oxides, quartz, and insoluble phosphates and sulfates.
Na_2O_2	600°	Ni; Ag, Au, Zr; Pt (<500 °C)	For sulfides; acid-insoluble alloys of Fe, Ni, Cr, Mo, W, and Li; Pt alloys; Cr, Sn, and Zn minerals.
H_3BO_3	250°	Pt	For analysis of sand, aluminum silicates, titanite, natural aluminum oxide (corundum), and enamels.
$Na_2B_4O_7$ (878°)	1,000-1,200°	Pt	For Al_2O_3; ZrO_2 and zirconium ores, minerals of the rare earths, Ti, Nb, and Ta, aluminum-containing materials; iron ores and slags.
$Li_2B_4O_7$ (920°) or $LiBO_2$ (845°)	1,000-1,100°	Pt, graphite	For almost anything except metals and sulfides. The tetraborate salt is especially good for basic oxides and some resistant silicates. The metaborate is better suited for dissolving acidic oxides such as silica and TiO_2 and nearly all minerals.
NH_4HF_2 (125°) NaF (992°) KF (857°) or KHF_2 (239°)	900°	Pt	For the removal of silicon, the destruction of silicates and rare earth minerals, and the analysis of oxides of Nb, Ta, Ti, and Zr.

Source: Dean (1995) and Bock (1979).

Preconcentration techniques

- Volatilitation & destillation (I, Ru, Po, Ni, Tc etc) – limited nr of elements
- Precipitation and co-precipitation techniques.

TABLE 14.13 — Common coprecipitating agents for radionuclides[1]

Radionuclide	Oxidation State	Coprecipitate	Carrier[2]	Notes
Am	+3	hydroxide	Am^{+3}, Fe^{+3}	
		iodate	Ce^{+4}, Th^{+4}, Zr^{+4}	
		fluoride, oxalate, phosphate, hydroxide	La^{+3}, Ce^{+3}, Nd^{+3}, Bi^{+3}	
		oxalate	Ca^{+2}	
		acetate	Am^{+4}	
		fluoride, sulfate	La^{+3}	
		acetate	UO_2^{+2}	
Cs	+1	phosphomolybdate, chloroplatinate, bismuth nitrate, silicomolybdate	Cs^{+1}	
Co	+2	hydroxide	Co^{+2}	
		potassium cobalt nitrate	Co^{+2}	
		1-nitroso-2-napthol	Co^{+2}	
		sulfide	Co^{+2}	
Fe	+3	hydroxide	Fe^{+3}	
		ammonium pyrouranate	Fe^{+3}	
I	−1	iodide	Pb^{+2}, Ag^{+1}, Pd^{+2}, Cu^{+2}	
Ni	+2	dimethylglyoxime hydroxide	Ni^{+2}	
Nb	(V)	hydroxide, phosphate	Nb(V)	
Np	+4	phosphate	Ca^{+2}	
Po	+4	tellurium	Te	Tellurate reduced with $SnCl_2$
		tellurate	Pb^{+2}	
		selenium	Se or Se^{-2}	
		dioxide	Mn^{+4}	
		hydroxide	Fe^{+3}, Al^{+3}, La^{+3}	
		sulfide	Cu^{+2}, Bi^{+2}, Pb^{+2}	
Pu	+3	fluoride	La^{+3}, Nd^{+3}, Ce^{+3}, Ca^{+2}	
	+4	sulfate	$La^{+3}(K^{+1})$	
	(VI)	fluoride	La^{+3}, Nd^{+3}, Ce^{+3}	
		oxalate, iodate	Th^{+4}	
		phosphate	Zr^{+2}, Bi^{+3}	
		sodium uranylacetate	UO_2^{+2}	

Radionuclide	Oxidation State	Coprecipitate	Carrier[2]	Notes
Ra	+2	hydroxide sulfate, chromate, chloride, bromide oxalate, phosphate fluoride	Fe^{+3} Ba^{+2} Th^{+4}, Ca^{+2}, Ba^{+2} La^{+3}	
Sr	+2	carbonate nitrate chromate sulfate phosphate hydroxide	Sr^{+2}, Ba^{+2}, Ca^{+2} Sr^{+2}, Ba^{+2} Ba^{+2} Sr^{+2}, Ca^{+2}, Pb^{+2} Sr^{+2} Fe^{+3}	Alkaline pH
Tc	+4 (VII)	hydroxide chlorate, iodate, perruthenate, tetrafluoroborate sulfide	Tc^{+4}, Fe^{+3}, Mn^{+2} $(Phenyl)_4As^{+1}$ Tc^{+7}, Re^{+7}, Cu^{+2}, Cd^{+2}	
Th	+4	hydroxide fluoride iodate phosphate, peroxide sulfate oxalate	Th^{+4}, La^{+3}, Fe^{+3}, Zr^{+3}, Ac^{+3}, Zn^{+2} Th^{+4}, La^{+3}, Nd^{+3}, Ce^{+3} Th^{+4}, Zr^{+3} Th^{+4}, Bi^{+3} Ba^{+2} Ca^{+2}	
U	+4	cupferron, pyrophosphate, phosphate, iodate, sulfate, oxalate	U^{+4}	
		fluoride	La^{+3}, Nd^{+3}	
	(V)	phosphate	Zr^{+3}	
		sulfate	Ca^{+2}	
	(VI)	cupferron	U(VI)	Neutral solution
		pyrouranate	U(VI)	From aqueous NH_3, many ions stay in solution as NH_3 complex
		phosphate	U(VI), Al^{+3}	
		peroxide	U(VI)	Th^{+4}, Zr^{+3} also coprecipitate
		hydroxide	Fe^{+3}	Without carbonate
		fluoride	Th^{+4}	
Zr	+4	hydroxide	Fe^{+3}	

(1) Compiled from: Anders, 1960; Booman and Rein, 1962; Cobble, 1964; EPA, 1973; 1980; 1984; DOE, 1990, 1995, 1997; Finston and Kinsley, 1961, Grimaldi, 1961; Grindler, 1962; Hyde, 1960; Kallmann, 1961; Kallmann, 1964; Kirby and Salutsky, 1964; Metz and Waterbury, 1962; Sedlet, 1964; Sundermann and Townley, 1960; and Turekian and Bolter, 1966.

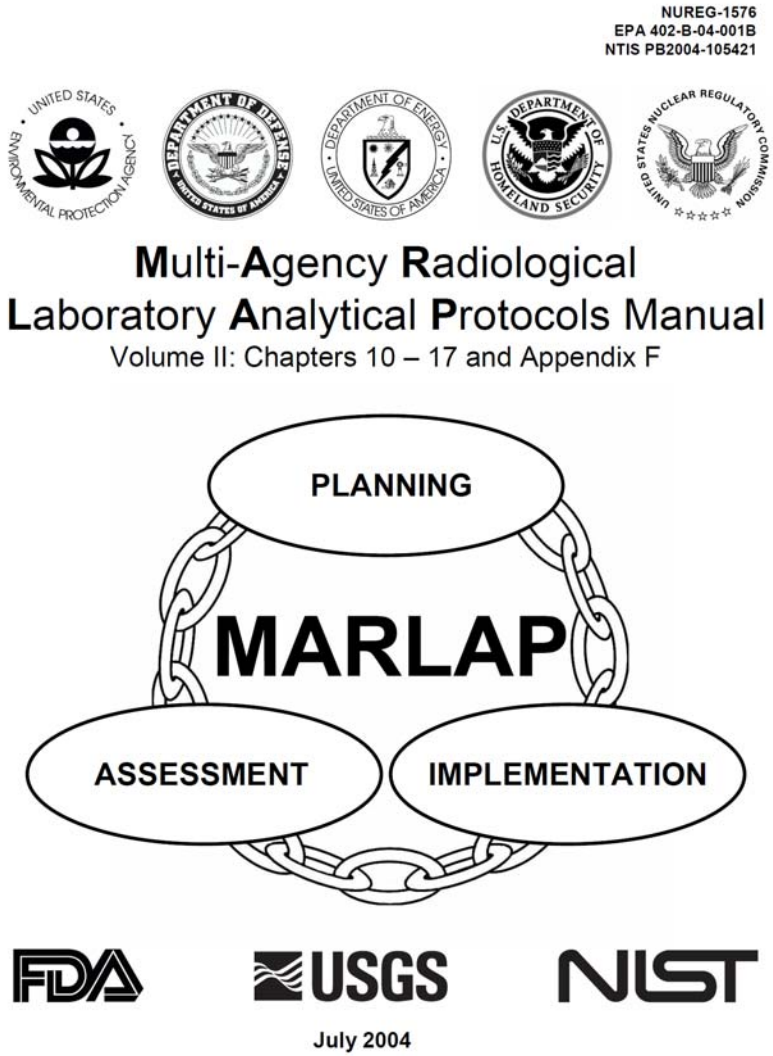
(2) If the radionuclide itself is listed as the carrier, a different isotope would be used to assess recovery.

TABLE 14.14 — Coprecipitation behavior of plutonium and neptunium

Carrier Compound	Pu^{+3}	Pu^{+4}	Pu(VI)	Np^{+4}	Np(V)	Np(VI)
Hydroxides	C	C	C	C	C	C
Calcium fluoride	C	C		C		
Lanthanum fluoride	C	C	NC	C	C	NC
Barium sulfate	C	C	NC	C	NC	NC
Phosphates:						
Calcium phosphate	C	C		C		
Bismuth phosphate	C	C		C	NC	NC
Zirconium phosphate	NC	C	NC	C	NC	NC
Thorium pyrophosphate	NC	C	NC			
Thorium hypophosphate		C	NC			
U^{+4} hypophosphate		C	NC			
Oxalates:						
Lanthanum oxalate	C	C	NC	NC		
Bismuth oxalate	C	C	NC			
Thorium oxalate	C	C	NC	C		
U^{+4} oxalate	C	C	NC			
Iodates:						
Zirconium iodate		C	NC	C		
Ceric iodate		C	NC	C		
Thorium iodate		C	NC	C		NC
Sodium uranyl acetate	NC	NC	C	NC	Poor	C
Zirconium phenylarsenate	NC	C	NC	C	Poor	NC
Thorium peroxide		C		C		
Bismuth arsenate		C	NC	C		

"C" indicates nearly quantitative coprecipitation under proper conditions; "NC" indicates that coprecipitation can be made less than 1–2 percent under proper conditions. [Data compiled from Seaborg and Katz, Korkisch (1969), and the NAS-NS 3050, 3058 and 3060 monographs.]

MARLAP-manual from US EPA



http://www.epa.gov/rpdweb00/marlap/manual.html